Near Zero Emissions Oxy-combustion Flue Gas Purification

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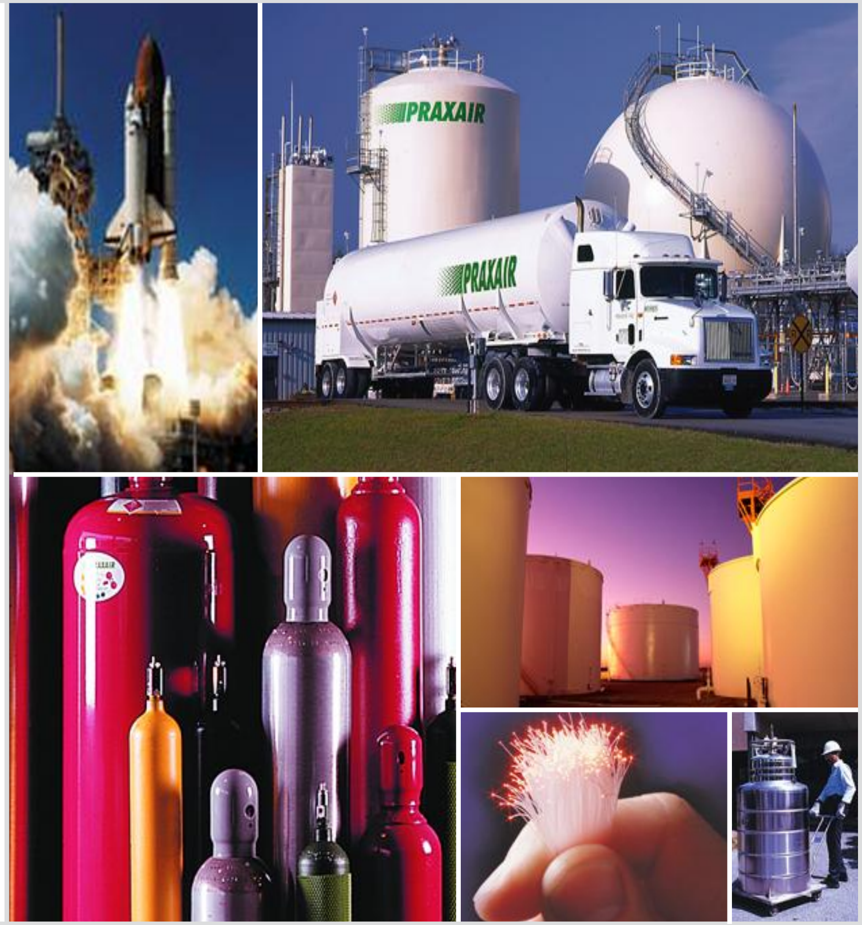

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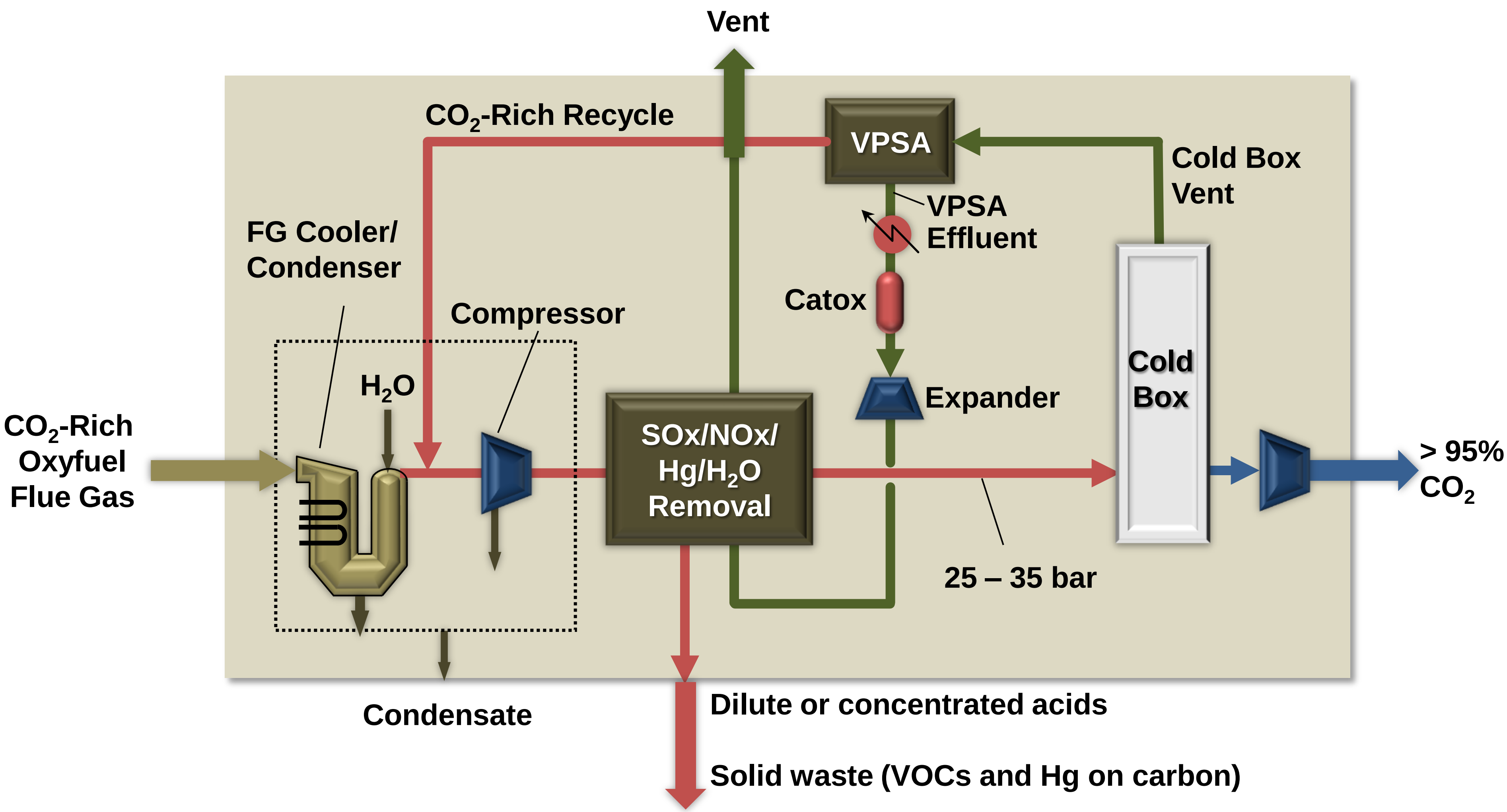
Praxair At A Glance

- **A Fortune 300 company with 2009 sales of $9 Bn**
- **One of the largest industrial gases companies in the world**
- **Markets served**
  - Metals, Energy, Chemicals, Healthcare, Electronics, Manufacturing, Food and Beverage, Aerospace and various other markets
- **Major gas products**
  - Atmospheric gases: O_2, N_2, rare gases (Ar, Xe, Kr, Ne)
  - Process Gases: H_2, CO_2, He, acetylene
  - Specialty Gases
- **Experience with several technologies applicable to CCS**
  - Cryogenic, adsorption and polymeric-membrane air separation
  - Hydrogen production
  - Carbon dioxide purification and liquefaction
  - Oxy-fuel combustion

Project Overview

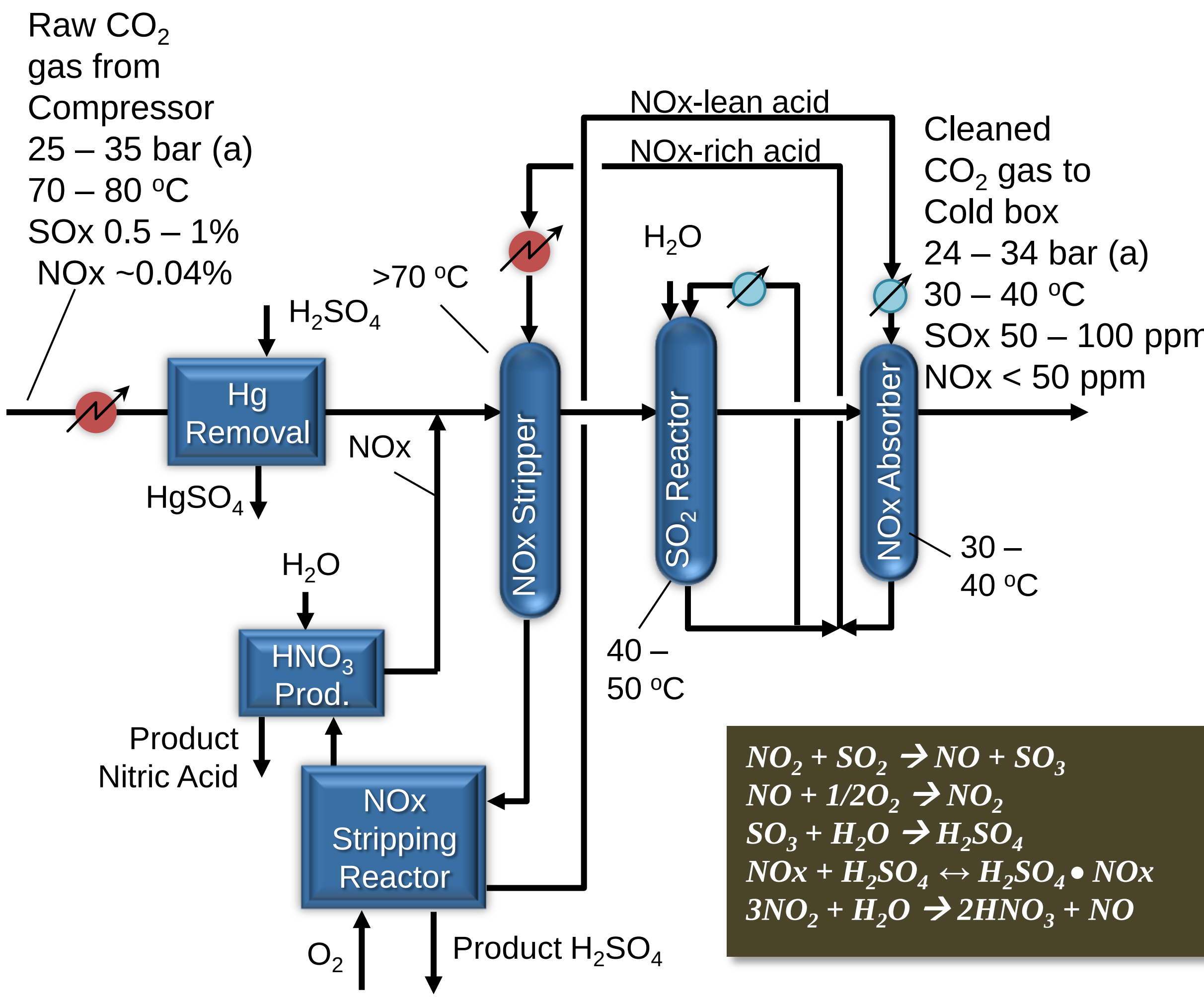
- **Goal: Develop a near-zero emissions oxy-combustion flue gas purification technology**
  - >95% CO_2 capture for existing plants with high air ingress
  - Produce high purity CO_2 by removing >90% of SOx/NOx/Hg
- **Total cost: $5.4MM**
  - DOE $3.24 MM
  - Praxair $2.16 MM
- **DOE Project # NT0005341**
  - DOE Program manager – Mike Mosser
- **Project performance dates: 1/1/09 – 12/31/11**
- **Project participants**
  - Praxair
  - Foster Wheeler
  - AES
  - WorleyParsons Canada

Technology Fundamentals
Near Zero Emissions CO_2 Processing Unit (CPU)



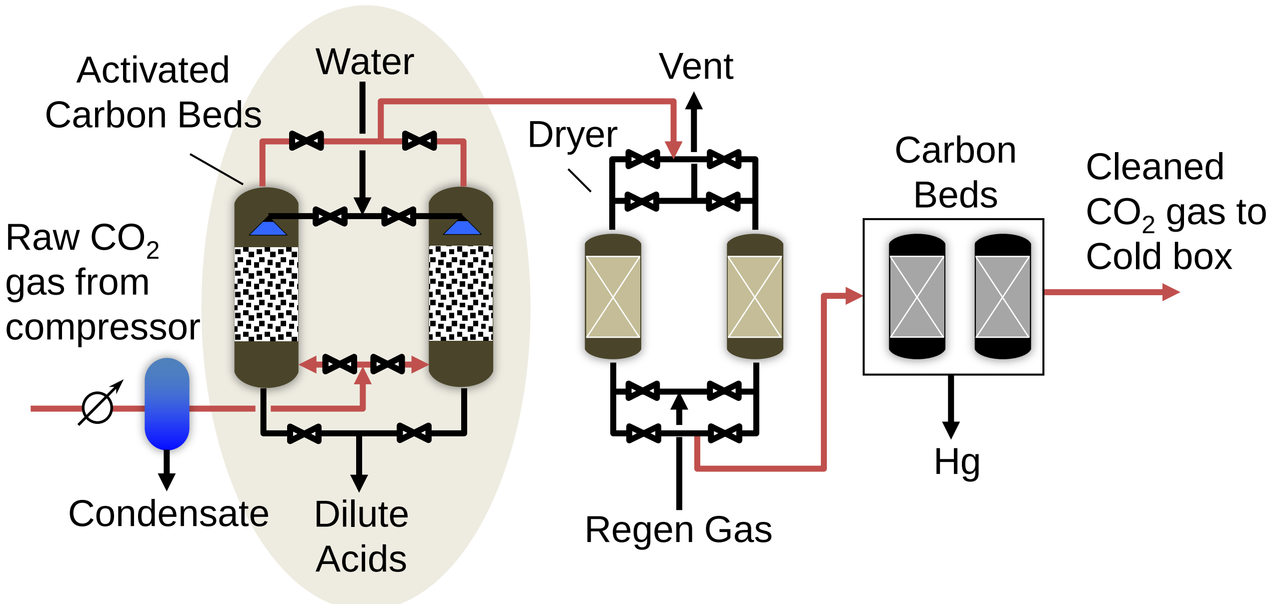
Technology Fundamentals
Sulfuric Acid Process for SOx/NOx/Hg Removal

- **Modified lead chamber process**
- **SOx and NOx are converted to saleable acids**
- **Recirculation of NOx using NOx absorber and NOx stripper aids the SO_2 oxidation reaction**



$NO_2 + SO_2 \rightarrow NO + SO_3$
$NO + 1/2O_2 \rightarrow NO_2$
$SO_3 + H_2O \rightarrow H_2SO_4$
$NOx + H_2SO_4 \leftrightarrow H_2SO_4 \bullet NOx$
$3NO_2 + H_2O \rightarrow 2HNO_3 + NO$

Technology Fundamentals
Activated Carbon Process for SOx/NOx/Hg Removal



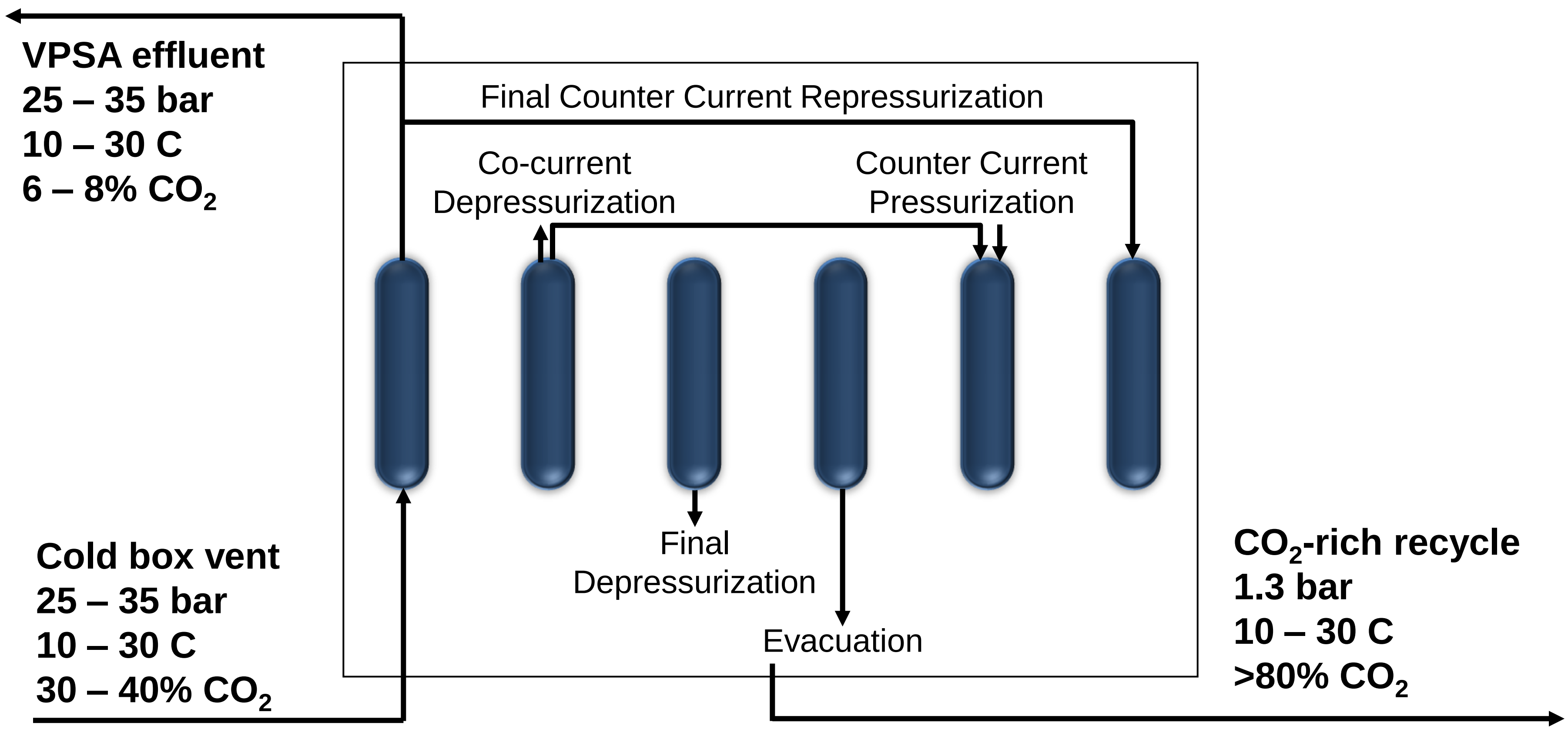
$SO_2 + 1/2O_2 \rightarrow SO_3$
$NO + 1/2O_2 \rightarrow NO_2$
$SO_3 + H_2O \rightarrow H_2SO_4$
$3NO_2 + H_2O \rightarrow 2HNO_3 + NO$

- **SO_2 and NO are oxidized and retained on activated carbon**
- **Carbon is regenerated by water wash followed by drying**
- **Dilute acid stream is produced**

Technology Fundamentals
VPSA (Vacuum Pressure Swing Adsorption)

PRAXAIR

- Multi-bed adsorption unit for separating CO_2 from cold box vent stream
- Simple cycle with minimum rotating equipment
- Shallow evacuation level



Benefits of Proposed Technologies

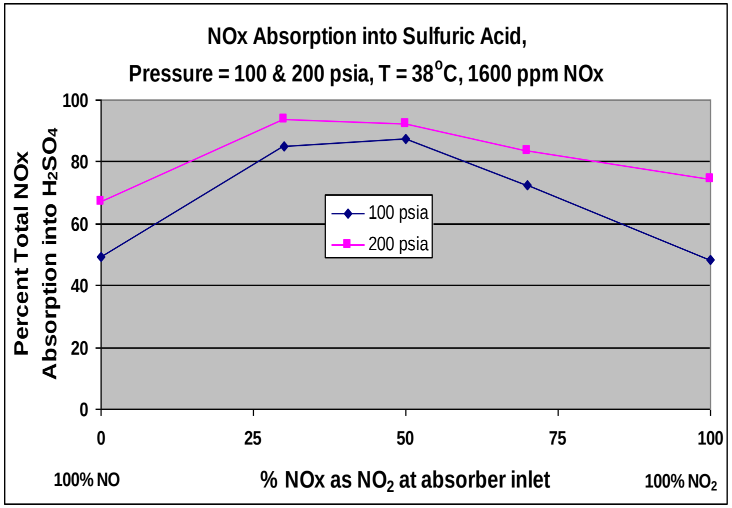
- **Near zero stack emissions**
- **High CO_2 recovery**
  - >95% for old plants with 10% air ingress
  - >99% for new plants with 2% air ingress
- **High CO_2 purity**
- **Sulfuric acid process**
  - Lower FGD/SCR operating costs for existing plants
    - Reduce/eliminate limestone, power, gypsum disposal and ammonia costs
    - Generate revenue from by-products
  - Lower capital and operating costs for new plants
    - Much smaller vessel sizes
- **Activated carbon process**
  - Lower investment costs for new plants
- **Lower CO_2 capture costs; Maximum benefit realized when**
  - Existing plant does not have FGD/SCR and high purity CO_2 is desired → alternative option will require installation of FGD/SCR
  - Existing plant has high air ingress → alternative option will have poor CO_2 recovery

Key Challenges

- **Sulfuric acid process**
  - Maximum allowable SOx in boiler may significantly limit flue gas SOx levels
  - High pressure & high temperature
  - Technology development
  - Material of construction
  - Acid sales revenue will depend on product quality & proximity to customer
- **Activated carbon process**
  - Longevity of process performance
  - Disposal of dilute acid stream
- **VPSA**
  - Tolerance to residual SOx/NOx in cold box vent
- **Commercial viability**
  - Low efficiency of existing plants
  - Capital cost advantage compared to conventional technology
  - Adoption by power producers

Current Status
Sulfuric Acid Process

- **Bench-scale single column (1' L, 1.5" ID) unit**
  - Capacity – 0.06 tpd CO_2 in flue gas
  - Capable of testing different unit ops of the process
  - Synthetic flue gas contacted with circulating H_2SO_4
- **Gas phase nitric oxide (NO) oxidation kinetics confirmed**
- **NOx mass transfer in H_2SO_4 is being evaluated**
- **>90% NOx absorption in one stage; higher pressure and $NO:NO_2$ ratio close to 1:1 improved NOx absorption**
- **NOx removal from acid may be challenging**



Current Status
Activated Carbon Process

- **Two carbon materials selected based on SOx removal screening tests**
- **Bench-scale unit with one carbon bed (1’ L, 1” ID) built**
  - Capacity – 0.02 tpd CO_2 in flue gas
  - Synthetic flue gas is fed until breakthrough of SOx or NOx
- **Excellent simultaneous SOx/NOx removal achieved**
  - SO_2 >99 % and NOx >96 %
- **Performance enhanced by**
  - Lower temperature
  - Higher pressure
  - Presence of moisture

Current Status
VPSA

- **Bench-scale unit (0.03 tpd) built for screening adsorbents**
  - Three adsorbents selected based on cost, CO_2 recovery, CO_2 purity and vacuum pump size
- **Pilot unit with 12 vessels (L ~ 11’, ID ~ 2.5”) commissioned**
  - Capacity – cold box vent containing 0.3 tpd CO_2 (equiv. to 3 tpd CO_2 in FG)
- **First set of data meets/exceeds the VPSA performance targets**
  - 99% capture rate with VPSA + cold box

Current Status
Commercial Viability

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- **Design basis**
  - 460 MW (gross) subcritical plant
    - Site ambients: 11.3 psia, 87 F, 26% RH
    - Bituminous (high sulfur) and PRB (low sulfur) coals
    - Existing FGD and SCR for SOx/NOx control
    - 2% air ingress
  - Air separation unit producing 97% O_2
  - Two CO_2 processing unit (CPU) designs
    - CO_2 purified to >95% purity and compressed to 153 bar
    - Acid Process for Bituminous-derived flue gas
    - Activated carbon process for PRB-derived flue gas
    - VPSA included in both CPUs
- **Results**
  - > 99% reduction in stack emissions of CO_2 & pollutants and production of high purity CO_2 while reducing CO_2 capture costs by \$1 - \$3/ton compared to a conventional oxyfuel CO_2 purification process
  - Power plant efficiency drops by ~10 percentage points in both the cases

Current Status
Performance Projections – Near Zero Emissions

Coal	Bituminous				PRB			
SOx/NOx removal	Sulfuric Acid Process				Activated Carbon Process			
	Composition by volume			% Reductions in stack emissions	Composition by volume			% Reductions in stack emissions
Component	Flue gas	Vent stream	Product CO_2		Flue gas	Vent stream	Product CO_2	
CO_2	68.53 %	6.93%	96.93 %	98.8%	62.05 %	7.26%	96.92 %	98.9%
$N_2 + O_2 + Ar$	12.73%	92.86%	3.05%		10.58%	91.96%	3.08%	
H_2O	18.25 %	Nil	1 ppm		27.28 %	0.55%	1 ppm	
CO	284 ppm	<10 ppm	71 ppm	>99.5%	280 ppm	<10 ppm	83 ppm	>99.5%
SO_X	3884 ppm	Nil	68 ppm	>99.9%	471 ppm	Nil	7 ppm	>99.9%
NO_X	391 ppm	9 ppm	57 ppm	99.5%	156 ppm	7 ppm	5 ppm	99.6%
HCl	402 ppm	Nil	0 ppm	>99.9%	18 ppm	Nil	0 ppm	>99.9%
VOC	1.2 ppm	Nil	<0.1 ppm	>99.9%	1.3 ppm	Nil	<0.1 ppm	>99.9%
Hg	1.0 ppb	Nil	<0.1 ppb	>99.9%	10.1 ppb	Nil	<0.1 ppb	>99.9%

Stack Flow is ~98% (by wt.) Lower than Air-fired Operation

Future Plans

- **Sulfuric Acid Process**
  - Complete bench scale tests (Q4 2010) and issue a topical report (Q1 2011)
  - After successful completion, propose a new R&D program to conduct tests in a bench-scale unit (~0.1 tpd) that integrates all unit operations
- **Activated Carbon Process**
  - Complete long-term regenerability tests (Q4 2010)
  - Build and operate a dual bed continuous unit 2-5X the current unit (2011)
- **VPSA**
  - Bench-scale tests for SOx/NOx tolerance (Q2 2011)
  - Complete pilot tests (Q3 2011)
  - Develop a simulation tool to predict process performance (Q3 2011)
- **Commercial viability**
  - Technoeconomic analysis and operability assessment (Q3 2011)
- **Proposed commercialization timeline**
  - 10 – 50 tpd CPU demo with activated carbon & VPSA (2012 – 2013)
  - Ready for larger size units in 2015

Summary

- Promising results with activated carbon & VPSA processes
- Acid process next steps will be determined by year end
- Technology can achieve high CO_2 recovery, high purity CO_2 and near zero stack emissions while lowering capture costs
- Targeting 10 – 50 tpd demonstration in 2012 – 2013

Acknowledgement & Disclaimer

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